

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08G 18/28, 18/71, C09D 5/04		A1	(11) International Publication Number: WO 00/37520 (43) International Publication Date: 29 June 2000 (29.06.00)
(21) International Application Number: PCT/EP99/10180 (22) International Filing Date: 20 December 1999 (20.12.99)		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(30) Priority Data: 98204363.0 22 December 1998 (22.12.98) EP		Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): VAN HEUGTEN, Richard, Johannes, Marieke [NL/NL]; Broeke 5, NL-4617 NN Bergen op Zoom (NL). VAN DER SANDEN, Johannes, Bernardus [NL/NL]; Bergsebaan 23, NL-4709 AJ Nispen (NL). VIJVERBERG, Cornelis, Andrianus, Maria [NL/NL]; Goudenregenstraat 2, NL-4661 WK Halsteren (NL).			
(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).			

(54) Title: THIXOTROPIC AMINO FORMALDEHYDE RESIN**(57) Abstract**

The present invention relates to a thixotropic amino formaldehyde resin with a urea-functional compound, obtainable by adding a polyisocyanate-functional compound to a monoamine-functional compound or a monoisocyanate-functional compound to a polyamine-functional compound in the presence of the amino formaldehyde resin and reacting the amine and isocyanate-functional compounds to form the urea-functional compound entangled to the resin. The thixotropic amino formaldehyde resin can be used in the formulation of coating or adhesive compositions.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

THIXOTROPIC AMINO FORMALDEHYDE RESIN

5 The present invention relates to a thixotropic amino formaldehyde resin with a urea-functional compound and the use thereof in coating formulations.

Thixotropic agents or sag control agents are essential elements of nowadays-produced coating compositions. They not only provide a stable mixture of the 10 several components in a coating composition, but also enable the application of the coating, even in thick layers on vertically placed objects, without the occurrence of sags in the cured coating.

It is well known in the art to prepare a thixotropic binder composition, e.g., by 15 mixing a binder and a sag control agent. For example, in EP 0,198,519 a diurea compound is used as a sag control agent in a thixotropic coating composition. The preparation of the sag control agent may be carried out in the presence of a binder. In GB 1,454,414 a thixotropizing urea adduct is prepared *in situ* in the presence of the binder. In this publication it is further said that urea adducts 20 prepared *in situ* in the presence of an amino formaldehyde resin, readily show incompatibility with the resin. It is concluded that it is more effective to carry out *in situ* formation of the urea adduct in the plasticizing binder.

In GB 1,454,414 a general method is disclosed for the preparation of a thixotropic amino formaldehyde resin-containing coating composition, viz. *in situ* 25 formation of a urea adduct in the binder component and then mixing the thixotroped binder with the amino formaldehyde resin. Urea adducts are obtained by reacting an amine-functional compound and an isocyanate-functional compound. Substantially the same method is used in EP 0,198,519 wherein the binder is selected from ester diols, polyesters, polyurethanes, alkyd 30 resins, acrylate, and methacrylate resins. In DE 1,805,693 the formation of urea-functional compounds is described without the presence of any binder. The thus obtained thixotropic coating compositions based upon a thixotropic

binder and an amino formaldehyde resin are well known and used in the art.

However, in practice a large number of thixotropic coating compositions are used containing different binders. As a consequence the different binders 5 should all be modified with a thixotropic agent. Therefore, the use of a universal thixotropic amino formaldehyde resin would give a substantial advantage in the preparation of coating compositions.

Moreover, since *in situ* formation of a urea adduct in the binder component 10 limits the functionality of the binder component, e.g., the binder component should not be reactive towards the amine-functional compound or the isocyanate-functional compound which are used for the *in situ* formation of the urea adduct, there is a need for a thixotropic coating composition based upon a thixotropic amino formaldehyde resin.

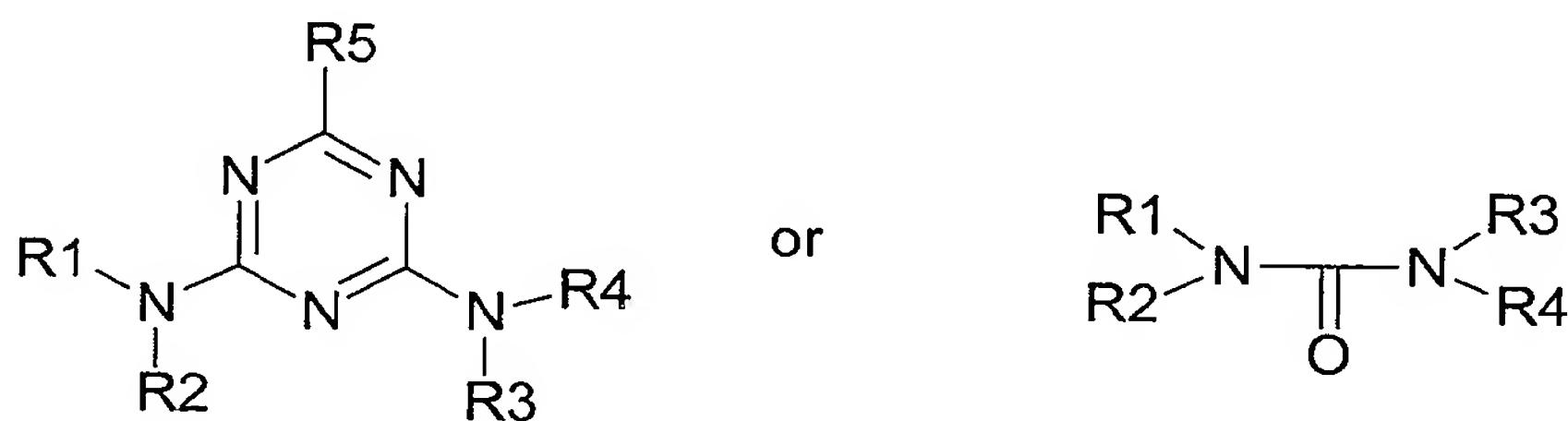
15

Surprisingly, it was found that a thixotropic amino formaldehyde resin with a urea-functional compound is obtained by adding a polyisocyanate-functional compound to a monoamine-functional compound or a monoisocyanate-functional compound to a polyamine-functional compound in the presence of 20 the amino formaldehyde resin and reacting the amine and isocyanate-functional compounds to form the urea-functional compound entangled as solid material in the resin. The thus obtained urea-adduct acts as a rheology modifier and a thixotropic effect is developed in the amino formaldehyde resin.

25 It was found that by the in-situ preparation of a urea compound from a monoamine and an polyisocyanate-functional compound first the free formaldehyde content is decreased and that after that, if the free formaldehyde content no longer decreases, a thixotropic effect is developed in the amino formaldehyde resin.

30 It was found that particularly good results were obtained when the amount of the isocyanate-functional compound is at least 4 times the amount of free formaldehyde that is present in the amino formaldehyde resin.

The process does not depend on the type of amino formaldehyde resin that is used. Resins with a relatively high or low free formaldehyde content can be used. However, preferably amino formaldehyde resins are used with a relatively low free formaldehyde content. In general, these amino formaldehyde resins 5 can be schematically indicated by the following chemical structure:



wherein each of R₁, R₂, R₃, and R₄ independently have the meaning of H, or CHR₆-O-R₇, wherein the R₆ and R₇ groups independently have the meaning of 10 H or alkyl. R₅ has the meaning phenyl or NR₈R₉, wherein R₈ and R₉ have the same meaning as R₁, R₂, R₃, or R₄.

In general, amino formaldehyde resins contain molecules of the above general formula and oligomers thereof.

15 In the context of this invention, a monoamine-functional compound is an amine compound, which contains only one isocyanate-reactive amino group. Suitable amine-functional compounds include primary amines, such as benzylamine, methylamine, ethylamine, n-propylamine, sec-propylamine, n-butylamine, sec-butylamine, tert-butylamine, n-pentylamine, α -methylbutyl-20 amine, α -ethylpropylamine, β -ethylbutylamine, hexylamine, octylamine, decylamine, stearylamine, cyclohexylamine, aniline, and mixtures thereof. The primary amines generally contain not more than 55 carbon atoms, preferably 1-24, and more particularly 1-12 carbon atoms. Amines containing one primary amino group and one or more ether and/or hydroxyl groups are 25 also applicable; for example, ethanolamine, 3-(dimethylamino)propylamine, 6-aminohexanol, p-methoxybenzylamine, methoxypropylamine, ethoxypropyl-

amine, 3,4-dimethoxyphenyl-ethylamine, 2,5-dimethoxyaniline, furfurylamine, tetrahydrofurfurylamine and bis(3-aminopropyl)-polytetrahydrofuran having a molecular weight of about 750. Preferred monoamines are selected from hexylamine, methoxypropylamine, ethoxypropylamine, benzylamine, or 5 mixtures thereof.

In the context of this invention, a polyamine-functional compound is an amine compound, which contains at least two isocyanate-reactive amino groups. Suitable polyamine compounds include primary polyamines as, e.g., 1,6-hexamethylene diamine, neopentyldiamine, 2-methyl-1,5-pentamethylene diamine, 10 ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene heptamine, 2-butyl-2-ethyl-1,5-pentane-diamine, diamines obtained from dimeric fatty acids preferably having at least 36 carbon atoms, isophorone diamine, meta-xylene diamine, xylylene diamine, and mixtures thereof.

15 The primary polyamines generally contain not more than 55 carbon atoms, preferably 1-24, and more particularly 1-12 carbon atoms. Amines containing at least two amino groups and one or more ether and/or hydroxyl groups are also applicable. Preferred polyamines are selected from 1,6-hexamethylene diamine, isophorone diamine, toluene diamine, or mixtures thereof.

20

In the context of this invention, monoisocyanate-functional compounds are isocyanates that contain only one amine-reactive isocyanate group.

Examples of monoisocyanate-functional compounds are those represented by the formula R-NCO wherein R represents a monovalent aliphatic hydrocarbon 25 group having 2 to 18 carbon atoms, a monovalent cycloaliphatic hydrocarbon group having 5 to 15 carbon atoms, a monovalent araliphatic hydrocarbon group having 7 to 15 carbon atoms, or a monovalent aromatic hydrocarbon group having 6 to 15 carbon atoms. Examples of organic monoisocyanates which are particularly suitable include methyl isocyanate, butyl isocyanate, 30 hexyl isocyanate, benzyl isocyanate, phenyl isocyanate, naphthalene isocyanate, biphenyl isocyanate, methoxypropyl isocyanate, and ethoxypropyl isocyanate, or mixtures thereof. Preferred monoisocyanate compounds are

selected from hexyl isocyanate, methoxypropyl isocyanate, ethoxypropyl isocyanate, benzyl isocyanate, or mixtures thereof.

In the context of this invention, polyisocyanate-functional compounds are 5 isocyanates, which contain at least two amine-reactive isocyanate groups.

Suitable polyisocyanate-functional compounds include aliphatic, cycloaliphatic, and aromatic isocyanates. The polyisocyanate-functional compound can be an aromatic, aliphatic, cycloaliphatic and/or araliphatic isocyanate-functional compound. The polyisocyanate-functional compound can be an isocyanurate, 10 uretdione, biuret, allophanate, an adduct of a polyol and a diisocyanate, NCO prepolymers, or mixtures thereof.

Examples of suitable isocyanates to be used as the polyisocyanate-functional compound or as starting materials for preparing an polyisocyanate-functional compound comprising an isocyanurate, biuret or uretdione structure include 15 organic polyisocyanates represented by the formula



wherein k is 2 or higher and R represents an organic group.

Examples of diisocyanate-functional compounds are those represented by the above formula wherein k is 2 and R represents a divalent aliphatic hydrocarbon 20 group having 2 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon group having 5 to 15 carbon atoms, a divalent araliphatic hydrocarbon group having 7 to 15 carbon atoms, or a divalent aromatic hydrocarbon group having 6 to 15 carbon atoms. Examples of the organic diisocyanates which are particularly suitable include ethylene diisocyanate, 1,3-propylene diisocyanate 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 2-methyl-1,5-diisocyanate pentane, 2-ethyl-1,4-diisocyanate butane, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 30 isophorone diisocyanate, toluene diisocyanate, bis-(4-isocyanatocyclohexyl)-methane, 1,3- and 1,4-bis(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, 1-methyl-2,4-diisocyanato cyclohexane, (5-isocyanato)-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane, xylene

diisocyanate, 1-methyl-2,4-diisocyanato benzene, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and -1,4-xylylene diisocyanate, 2,4- and 2,6-hexahydrotoluylene diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-toluylene diisocyanate, 2,4- and 4,4'-diphenylmethane diisocyanate, 1,5-diisocyanato naphthalene, norbornane 5 diisocyanate, and mixtures thereof. Aliphatic polyisocyanates containing 3 or more isocyanate groups such as 4-isocyanatomethyl-1,8-octane diisocyanate and aromatic polyisocyanate containing three or more isocyanate groups such as 4,4',4"-triphenylmethane triisocyanate, 1,3,5-triisocyanate benzene, polyphenyl polymethylene polyisocyanates obtained by phosgenating 10 aniline/formaldehyde condensates, and mixtures thereof may also be used.

Also the isocyanurate trimer of isophorone diisocyanate, biuret of hexamethylene diisocyanate, the isocyanurate of hexamethylene diisocyanate, the uretdion of isophorone diisocyanate, the uretdion of hexamethylene diisocyanate, the allophanate of hexamethylene diisocyanate, and mixtures 15 thereof can be used.

Isocyanate-functional compounds comprising an allophanate structure are prepared by the reaction of the above-mentioned organic polyisocyanates with a mono- or polyalcohol. Preferably, isocyanate-functional compounds comprising an allophanate structure are prepared from 1,6-hexamethylene 20 diisocyanate and/or isophorone diisocyanate reacted with an alcohol, preferably butanol.

Polyisocyanate adducts include the reaction product of 3 moles of m-tetramethylxylene diisocyanate with 1 mole of trimethylol propane, the reaction product of 3 moles of toluene diisocyanate with 1 mole of trimethylol propane. 25 Preferred polyisocyanate compounds are selected from 1,6-hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate, isocyanurate of hexamethylene diisocyanate, or mixtures thereof.

The reaction between the monoamine and the polyisocyanate-functional 30 compound or the monoisocyanate and polyamine-functional compound may generally be carried out in any arbitrarily chosen way by combining the reacting compounds, optionally at elevated temperature. It is preferred that the reaction

should be carried out in an atmosphere of an inert gas at temperatures in the range of -20° to +80°C.

The sequence in which the monoamine and the polyisocyanate-functional compound or the monoisocyanate and polyamine-functional compound are 5 added to the amino formaldehyde resin is not important. As a rule, it is preferred that the isocyanate-functional compound is added to the amine-functional compound that is present in the resin. If so desired, this may be done in several steps. However, if the poly- or monoisocyanate-functional compound is added first, care should be taken that the thus obtained mixture is not stored for too 10 long or at a too high temperature, since a reaction between the amino formaldehyde resin and the poly- or monoisocyanate-functional compound might occur.

Needless to say, the amine and the isocyanate-functional compounds should be thoroughly mixed with the amino formaldehyde resin upon addition, for instance, 15 by using low or high shear mixers (such as rotor-stator mixers, dispensers and the like). Preparation can be performed batchwise as well as in a continuous process.

It is also possible to add the amine compound to a portion of the amino formaldehyde resin and to add the isocyanate-functional compound to another 20 portion of the amino formaldehyde resin followed by combining the two amino formaldehyde resin mixtures, optionally with additional amino formaldehyde resin being added.

The reaction between the amine-functional compound and the isocyanate-functional compound is carried out in the amino formaldehyde resin, wherein 25 optionally an inert organic solvent can be present.

If the amine-functional compound and the isocyanate-functional compound are added in stoichiometric amounts, each amine group of the amine-functional compound reacts with an isocyanate group of the isocyanate-functional 30 compound and that no free amine or isocyanate groups are present after completion of the theoretical reaction. However, in order to prevent the presence of small amounts of unreacted amino groups of the amine-functional

compound a slight excess of isocyanate-functional compound can be used. Preferably, this excess ranges from 1 to 10%, based on equivalents.

Very good results are obtained by reacting a monoamine with a polyisocyanate

5 if the monoamine is hexylamine, benzylamine, methoxypropylamine, ethoxypropylamine or mixtures thereof, and the polyisocyanate-functional compound is a diisocyanate, in particular 1,6-hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate, the isocyanurate of hexamethylene diisocyanate, or mixtures thereof.

10 Very good results are obtained by reacting a monoisocyanate with a polyamine if the monoisocyanate is hexyl isocyanate, benzyl isocyanate, methoxypropyl isocyanate, ethoxypropyl isocyanate or mixtures thereof, and the polyamine-functional compound is a diamine, in particular 1,6-hexamethylene diamine, isophorone diamine, toluene diamine, or mixtures thereof.

15

Since the thixotropic amino formaldehyde resins according to the present invention have a (very) low free formaldehyde content, the resins are pre-eminently suited to be used in the formulation of coating compositions. In coating compositions these resins can be used as cross-linkers, e.g., for high

20 temperature curing coating compositions. One of their advantages over presently used coating formulations comprising an amino formaldehyde resin is the much lower formaldehyde emission during application of the coating.

Depending on the amino formaldehyde resin employed, any conventional compound can be used as binder resin. The thixotropic coating composition

25 may further contain usual adjuvants and additives for instance pigment dispersants, dyes, pigments, solvents and accelerators for the curing reaction.

The thixotropic coating composition may be applied to a substrate in any desired manner, for instance by rolling, spraying, brushing, sprinkling, casting, dipping or electrostatic spraying. The thixotropic coating composition may

30 further be cured or baked in the usual way, for instance at ambient temperatures or in an oven at the higher temperatures, for instance in the range of 80° to 250°C, over a period of 2 to 120 minutes.

The invention will be further illustrated with reference to the following examples. Needless to say, these are exemplified embodiments to which the invention is not limited.

5

Measuring methods

Determination of the urea compound

A well defined weight of the urea modified amino formaldehyde resin is mixed with 100 g of acetone and gently stirred until a homogeneous solution is 10 obtained. The solution is carefully filtered over a glass fiber filter that was accurately weighted in advance. Directly after filtration the solid urea material on the filter is washed with 150 ml of acetone. The filter is dried during 45 minutes at 107°C. Directly after drying the filter is weighted again. Then the amount of 15 urea compound is calculated and given as a percentage based on the modified amino formaldehyde resin.

Determination of the free formaldehyde content

The free formaldehyde content of an amino formaldehyde resin can be measured quantitatively by reacting the free formaldehyde in the resin with 20 sodium sulfite, followed by titration with sulfuric acid. In this way the amount of alkaline liberated by the reaction between formaldehyde and sodium sulfite can be determined quantitatively. The free formaldehyde contents mentioned in the text were all determined at 20°C. If the free formaldehyde content is determined at 0°C (according ISO 9020) lower free formaldehyde levels will be found. A 25 free formaldehyde content of 1 wt.% corresponds to 0.33 meq formaldehyde/g of resin.

Example 1

30 Into a one-liter reaction vessel equipped with an anchor stirrer and two dropping funnels were charged 700 g of Setamine® US-144 BB-60 (a melamine-formaldehyde resin, ex Akzo Nobel) with a free formaldehyde content of 0.37 wt.%. The temperature was brought to 30°C. Then 25.05 g of benzylamine were

added and mixed at 200 rpm for 15 minutes. Next the reaction vessel was cooled with ice water and 20.25 g of hexamethylene diisocyanate were added in two minutes at 750 rpm. After the addition, the reaction mixture was stirred for another 30 minutes at 750 rpm.

5 The obtained white solution contained 3.0% of a diurea compound. The free formaldehyde content was 0.00 wt.%.

Example 2

10 Into a one-liter reaction vessel equipped with a dissolver having a disc with a diameter of 60 mm and two dropping funnels were charged 600 g of Cymel 303 (a melamine-formaldehyde resin ex. Cytec Industries) with a free formaldehyde content of 0.42 wt.%. 33.6 g of isobutanol were added. The mixture was stirred during three minutes at 1700 rpm. 29.27 g of benzylamine were added and mixed at 1700 rpm for 5 minutes. Next 23.66 g of hexamethylene diisocyanate

15 were added in six minutes at 2000 rpm. During the addition of the hexamethylene diisocyanate the stirrer speed was raised to 4400 rpm, the temperature raised to 61°C. After completion of the addition the reaction mixture was stirred for another 10 minutes at 4400 rpm. In this period the temperature raised to 78°C. The solution contained 7.1 wt.% of a diurea compound. The free

20 formaldehyde content was 0.07 wt.%.

Example 3

25 Into a one-liter reaction vessel equipped with an anchor stirrer and two dropping funnels were charged 700 g of Setamine® US-138 BB-70 (a butylated melamine resin, ex Akzo Nobel) with a free formaldehyde content of 1.34 wt.%. The temperature was raised to 30°C. Then 13.0 g of benzylamine were added and mixed at 200 rpm for 15 minutes. Next the reaction vessel was cooled with ice water and 10.5 g of hexamethylene diisocyanate were added during two minutes at 750 rpm. After the addition the reaction mixture was stirred for

30 another 30 minutes at 750 rpm.

A clear solution without solid diurea particles was obtained with a free formaldehyde content of 0.20 wt.%.

Claims

1. A thixotropic amino formaldehyde resin with a urea-functional compound obtainable by adding a polyisocyanate-functional compound to a 5 monoamine-functional compound or a monoisocyanate-functional compound to a polyamine-functional compound in the presence of the amino formaldehyde resin and reacting the amine and isocyanate-functional compounds to form the urea-functional compound entangled as solid material in the resin.
- 10 2. The thixotropic amino formaldehyde resin of claim 1 wherein the amount of the urea-functional compound is at least 4 times the amount of free formaldehyde that is present in the amino formaldehyde resin.
- 15 3. The thixotropic amino formaldehyde resin of claim 1 or 2 wherein the monoamine-functional compound is selected from hexylamine, methoxypropylamine, ethoxypropylamine, benzylamine, or mixtures thereof, and the polyisocyanate-functional compound is selected from 1,6-hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate, isocyanurate of hexamethylene diisocyanate, or mixtures thereof.
- 20 4. The thixotropic amino formaldehyde resin of any one of claims 1-3 wherein the monoisocyanate-functional compound is selected from hexyl isocyanate, methoxypropyl isocyanate, ethoxypropyl isocyanate, benzyl isocyanate, or mixtures thereof, and the polyamine is selected from 1,6-hexamethylene diamine, isophorone diamine, toluene diamine, or mixtures thereof.
- 25 5. A process for the preparation of a thixotropic amino formaldehyde resin with a urea-functional compound comprising the steps wherein a polyisocyanate-functional compound is added to a monoamine-functional compound or a monoisocyanate-functional compound is added to a

polyamine-functional compound in the presence of the amino formaldehyde resin, and is reacted to form the urea-functional compound entangled to the resin.

- 5 6. A coating or adhesive composition comprising the thixotropic amino formaldehyde resin of any one of claims 1-4.
7. A method of cross-linking a high temperature-curing coating composition by using the amino formaldehyde resin of any one of claims 1-4.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/10180

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/28 C08G18/71 C09D5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 23 59 929 A (AUGUST MERCKENS) 12 June 1974 (1974-06-12) page 3, line 30 -page 27, line 5; claims 1-8; examples 10,11 ---	1,3-6
X	DE 18 05 693 A (ARMOUR INDUSTRIAL CHEMICAL) 26 February 1970 (1970-02-26) page 2, line 13 -page 6, line 3; claims 1-8 ---	1,3
X	EP 0 198 519 A (AKZO) 22 October 1986 (1986-10-22) page 2, column 1, line 22 -page 4, column 5, line 28; claims 1-4; examples ---	1 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the International search

14 April 2000

Date of mailing of the international search report

27/04/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bourgonje, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/10180

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 300 388 A (BASF) 25 January 1989 (1989-01-25) page 2, column 1, line 33 -page 4, column 6, line 7; claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/10180

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE 2359929	A 12-06-1974	AT 331934	B	25-08-1976
		AT 331932	B	25-08-1976
		AT 331933	B	25-08-1976
		AT 326793	B	29-12-1975
		AT 274173	A	15-12-1975
		BE 808466	A	29-03-1974
		BE 808467	A	29-03-1974
		CA 1006283	A	01-03-1977
		CA 1006284	A	01-03-1977
		DE 2359923	A	20-06-1974
		DE 2360019	A	12-06-1974
		FR 2327295	A	06-05-1977
		FR 2327296	A	06-05-1977
		GB 1454388	A	03-11-1976
		GB 1454414	A	03-11-1976
		IT 1005517	B	30-09-1976
		IT 1005518	B	30-09-1976
		JP 49099131	A	19-09-1974
		JP 49099132	A	19-09-1974
		NL 7316870	A, B,	13-06-1974
		NL 7316873	A	13-06-1974
		US 4383068	A	10-05-1983
		US 3893956	A	08-07-1975
		AT 1049372	A	15-12-1975
		AT 1049472	A	15-12-1975
		AT 1049672	A	15-03-1975
DE 1805693	A 26-02-1970	FR 1591172	A	27-04-1970
		GB 1214556	A	02-12-1970
		US 3547848	A	15-12-1970
EP 198519	A 22-10-1986	NL 8500476	A	16-09-1986
		AT 49415	T	15-01-1990
		AU 572383	B	05-05-1988
		AU 5377086	A	28-08-1986
		BR 8600700	A	29-10-1986
		CA 1282890	A	09-04-1991
		CN 1006712	B	07-02-1990
		ES 552167	D	01-04-1988
		ES 8802176	A	16-06-1988
		JP 1926538	C	25-04-1995
		JP 6051851	B	06-07-1994
		JP 61192774	A	27-08-1986
		US 4851294	A	25-07-1989
		ZA 8601280	A	29-10-1986
EP 300388	A 25-01-1989	DE 3724555	A	02-02-1989
		AT 80904	T	15-10-1992
		DE 3874831	A	29-10-1992
		ES 2045025	T	16-01-1994
		US 4882408	A	21-11-1989